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TITLE : PRODUCTION OF LIGHT TRANSMISSIVE YTTRIUM-ALUMINUM-GARNET SINTERED BODY

ABSTRACT : PURPOSE: To improve light transmissivity by mixing a high purity Al_2O_3 powder with Y_2O_3, pulverizing after calcined at a prescribed temp., molding the mixture powder and firing at a specific temp. in a reducing atmosphere.

CONSTITUTION: The Al_2O_3 powder and Y_2O_3, each of which has ≥99.9% purity and ≥5m^2/g BET surface area are blended and mixed in a prescribed weight ratio and calcined at 1000-1600°C for 0.5 hour or more. The calcined powder is pulverized to ≤2μm and molded into a molded body having ≥2.1g/cm^3 raw density by a cold isostatic press or the like. Next, the molded body is fired in a N_2 atmosphere or a vacuum atmosphere of ≥1×10^{-2} degree of the vacuum at 50-300°C/hour temp. rising rate at 1600-1900°C for 2-20 hours to obtain the light transmissive Y-Al-garnet ($Y_3Al_5O_{12}$) sintered body having ≥70% linear light transmissivity in visible ray region.

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(54)【発明の名称】　透光性イットリウムーアルミニウムーガーネット焼結体の製造方法

(57)【要約】

【構成】それぞれ純度が９９．９％以上、ＢＥＴ比表面積５m^2／ｇ以上のAl_2O_3粉末とY_2O_3粉末を、Al_2O_3：Y_2O_3が０．４３：０．５７となるように調製し、混合した後、１０００～１６００℃で仮焼し、これを粉砕して原料粉末とし、この原料粉末を所定形状に成形した後、この成形体を真空度１×10^{-3} torr以上の真空雰囲気において、１６００～１９００℃で所定時間焼成する。真空雰囲気で焼成する代わりに、水素雰囲気或いは窒素雰囲気等の還元性雰囲気で焼成しても良い。

【効果】可視光領域の直線透過率を７０％以上とすることができ、時計用窓材、ランプ管、装飾品等に最適な材料を提供することができる。

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【特許請求の範囲】

【請求項1】純度がそれぞれ99．9%以上のAl₂O₃粉末とY₂O₃粉末を混合した後、1000～1600℃で仮焼し、これを粉砕して原料粉末とし、この原料粉末を所定形状に成形した後、還元性雰囲気中において、1600～1900℃の温度で焼成することを特徴とする透光性イットリウムーアルミニウムーガーネット焼結体の製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、透光性に優れた透光性イットリウムーアルミニウムーガーネット（以下、YAGという）焼結体の製造方法に関するもので、特に、可視光領域の直線透過率が70%を達成することができる透光性YAG焼結体の製造方法に関するものである。

【0002】

【従来技術】従来、YAG（$Y_3Al_5O_{12}$）は結晶型が立方晶であるため、粒界散乱が起こりにくく透明体として良好であるため、各種の製法により透光性焼結体を得る試みがなされている。

【0003】このようなYAGは、単結晶により作成する方法、Al₂O₃粉末とY₂O₃粉末をHIP処理やホットプレス焼成する方法、イットリウムイオンとアルミニウムイオンの尿素沈澱法等により製造されている（例えば、特公昭54－8369号公報）。

【0004】

【発明が解決しようとする問題点】しかしながら、単結晶合成では高価であり、任意の形状に製作することが困難であるという問題があった。また、HIP処理による場合には装置が大きくなり、生産性が良くないという問題があった。さらに、ホットプレスにより製造する場合には、成形型に用いるカーボンから焼結体に炭素が入り、透明度が下がるという欠点があった。

【0005】また、尿素沈澱法では、アンモニア蒸気の処理が必要であり、環境に悪影響を与える虞があった。

【0006】

【問題点を解決するための手段】本発明者等は、このような問題点に対して充分に検討を行った結果、Al₂O₃粉末とY₂O₃粉末を混合した後、仮焼し、粉砕したものを原料粉末として使用することで、従来のようなHIP処理、ホットプレス、尿素沈澱法を用いなくても良好な透光性焼結体を得ることができることを見出し、本発明に至った。

【0007】即ち、本発明の透光性YAG焼結体の製造方法は、純度がそれぞれ99．9%以上のAl₂O₃粉末とY₂O₃粉末を混合した後、1000～1600℃で仮焼し、これを粉砕して原料粉末とし、この原料粉末を所定形状に成形した後、還元性雰囲気中において、1600～1900℃の温度で焼成する方法である。

【0008】ここで、純度がそれぞれ99．9%以上のAl₂O₃粉末とY₂O₃粉末を使用するのは、純度が99．9%よりも低いと焼結体中に不純物が存在し、その透光性が低下するからである。

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【0009】また、Al₂O₃粉末とY₂O₃粉末の混合粉体を1000～1600℃で仮焼するのは、この仮焼によりある程度（10～50%程度）のYAG化を生じさせ、YAGの異常粒成長を抑制し、活性化を保持するためである。よって、仮焼温度が1000℃よりも低いとYAG化が生じ難く、1600℃よりも高いと活性化が低下し、緻密な焼結体を作成することができず、或いは、粉砕に長時間を要するようになるからである。そして、仮焼により、Al₂O₃粉末とY₂O₃粉末の混合粉末からYAMへ、YAMからYAGへ結晶が変化するが、仮焼することにより、YAMからYAGへ変化する際の体積膨張を生じさせ、成形後の焼成では体積膨張を生じさせずに焼結させ、これにより、焼結体中のボイドや欠陥の発生を抑制し、均一な焼結体を作成するためである。

【0010】また、1600～1900℃の温度で焼成するのは、1600℃よりも低い温度で焼成すると、焼結が不十分であり緻密化せず透光性が低下するからであり、1900℃よりも高い温度で焼成すると、異常粒成長が生じ、気孔を粒内に取り込んでしまい透光性が低下するからである、また、YAGの蒸発が生じ均質な焼結体を作成することができなくなるからである。

【0011】さらに、還元性雰囲気中で焼成するのは、大気中に比べH_2　やN₂は拡散が速いため、焼結体の緻密化を容易に達成することができるからである。真空焼成も同様な理由で良好である。

【0012】本発明のYAG焼結体は、例えば、それぞれ純度が99．9%以上、BET比表面積5m²／g以上のAl₂O₃粉末とY₂O₃粉末を、Al₂O₃：Y₂O₃が0．43：0．57となるように調製し、混合した後、1000～1600℃で0．5時間以上、好ましくは2時間程度仮焼する。仮焼は、完全にYAG化する前の段階、即ち、YAMやYAGが混在した状態まで反応させる。Al₂O₃粉末，Y₂O₃粉末の粒径は、YAGの異常粒成長を防止するためそれぞれ2μm以下であることが好ましい。

【0013】そして、これを粉砕して原料粉末とし、この原料粉末に所定の溶媒を添加し、これをポットミル，回転ミル等で混合粉砕する。仮焼粉末の粒子は2μm以下、好ましくは1μm以下であることが望ましい。この後、これを乾燥した後、80メッシュパスで整粒する。これを所望の成形手段、例えば、金型プレス，冷間静水圧プレス，押出し成形等により任意の形状に成形する。例えば、金型プレスによる場合には、2．5ton／cm³ 以上で行い、生成形体の密度をできるだけ上げる。成形体の生密度は、焼結体中のボイドを最小限に抑制するため2．1g／cm³ 以上となることが好ましい。

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試料No.	仮焼温度(℃)	焼成温度(℃)	焼成時間(時間)	昇温速度(℃/H)	焼成雰囲気	直線透過率(%)
＊1	——	1750	2	300	真空	52
2	1000	1750	2	300	真空	74
3	1300	1800	5	50	真空	76
4	1350	1600	20	100	真空	70
5	1350	1700	5	300	真空	77
6	1350	1750	2	300	真空	73
7	1350	1750	2	200	真空	75
8	1350	1750	2	100	真空	70
9	1350	1750	2	300	H_2	75
10	1350	1900	2	100	真空	74
11	1500	1750	2	300	真空	75
12	1600	1750	5	100	N_2	70
13	1600	1800	5	200	真空	70
＊14	800	1750	2	300	真空	55
＊15	——	1750	2	200	O_2	0.8

＊印は本発明の範囲外の試料を示す。

【0022】この実験結果より；本発明のＹＡＧ焼結体は可視光領域の直線透過率が７０％以上と優れた透光性を有することが判る。尚、試料No.１，１５は仮焼することなく、Al_2O_3 粉末と Y_2O_3 粉末を焼成した例である。また、表１中の昇温速度は、試料No.４を除き、１６５０℃までの昇温速度である。また、本発明者等は仮焼を１６５０℃で行う実験を行ったが、この場合には仮焼後回転ミルで粉砕できなかった。さらに、焼成を１９５０℃で行う実験を行ったが、試料は溶解して冷却中に割れを生じた。

【0023】

【発明の効果】以上詳述した通り、本発明の透光性ＹＡＧ焼結体の製造方法では、Al_2O_3 粉末と Y_2O_3 粉末を混合した後１０００～１６００℃で仮焼し、この後還元性雰囲気中において１６００～１９００℃の温度で焼成したので、１０００～１６００℃の仮焼によりＹＡＭからＹＡＧへ変化する際の体積膨張を生じさせることができ、成形後の焼成では体積膨張が生じることがなく、これにより、焼結体中のボイドや欠陥の発生を抑制し、均一な焼結体を作成することができる。これにより、可視光領域の直線透過率を７０％以上とすることができ、時計用窓材，ランプ管，装飾品等に最適な材料を提供することができる。

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CLAIMS

[Claim(s)]
[Claim 1] Purity is 99.9% or more of aluminum 2O3, respectively. Powder and Y2 O3 The manufacture approach of the translucency yttrium aluminum garnet sintered compact characterized by calcinating at the temperature of 1600-1900 degrees C in a reducing atmosphere after carrying out temporary quenching at 1000-1600 degrees C, grinding this, considering as raw material powder after mixing powder, and fabricating this raw material powder in a predetermined configuration.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the manufacture approach of a translucency YAG sintered compact that the straight-line permeability of a light field can attain 70%, especially about the manufacture approach of a translucency yttrium aluminum garnet (henceforth YAG) sintered compact excellent in translucency.
[0002]
[Description of the Prior Art] The former and YAG (Y3 aluminum 5O12) Since a crystal mold is a cubic, since it is good as the transparent body, the attempt which obtains a translucency sintered compact by various kinds of processes is made that grain boundary dispersion cannot take place easily.
[0003] Such YAG is the approach and aluminum 2O3 which are created with a single crystal. Powder and 2OY3 powder are manufactured with HIP processing, an approach, a urea precipitation method of yttrium ion and aluminum ion which carries out hotpress baking, etc. (for example, JP,54-8369,B).
[0004]
[Problem(s) to be Solved by the Invention] However, in single crystal composition, there was a problem that it was expensive and it difficult to manufacture in the configuration of arbitration. Moreover, when based on HIP processing, equipment became large, and there was a problem that productivity was not good. Furthermore, when manufacturing with a hotpress, carbon went into the sintered compact from the carbon used for a die, and there was a fault that transparency fell.
[0005] Moreover, in a urea precipitation method, an ammonia steam needs to be processed and there was a possibility of having a bad influence on an environment.
[0006]
[Means for Solving the Problem] this invention person etc. is aluminum 2O3, as a result of fully inquiring to such a trouble. Powder and Y2 O3 After mixing powder, it resulted in a header and this invention that a good translucency sintered compact could be obtained by using what carried out temporary quenching and was ground as raw material powder even if it does not use HIP processing like before, a hotpress, and a urea precipitation method.
[0007] That is, for the manufacture approach of the translucency YAG sintered compact of this invention, purity is 99.9% or more of aluminum 2O3, respectively. Powder and Y2 O3 After carrying out temporary quenching at 1000-1600 degrees C, grinding this, considering as raw material powder, after mixing powder, and fabricating this raw material powder in a predetermined configuration, it is the approach of calcinating at the temperature of 1600-1900 degrees C in a reducing atmosphere.
[0008] Here, purity is 99.9% or more of aluminum 2O3, respectively. Powder and Y2 O3 It is because an impurity will exist and the translucency will fall into a sintered compact, if using powder has purity lower than 99.9%.
[0009] Moreover, aluminum 2O3 Powder and Y2 O3 Temporary quenching of the powdered mixed fine particles is carried out at 1000-1600 degrees C for producing a certain amount of (about 10 - 50%) YAG-ization by this temporary quenching, controlling abnormality grain growth of YAG, and holding

activation. Therefore, it is because activation cannot fall if higher than 1600 degrees C, a precise sintered compact cannot be created [if temporary-quenching temperature is lower than 1000 degrees C, it will be hard to produce YAG-ization, and] or grinding comes to take a long time. And it is aluminum 2O3 by temporary quenching. Although a crystal changes from the mixed powder of powder and 2OY3 powder to YAM from YAM to YAG, By carrying out temporary quenching, it is for making it sinter without producing the cubical expansion at the time of changing from YAM to YAG, and producing cubical expansion in baking after shaping, and this controlling the void in a sintered compact, and generating of a defect, and creating a uniform sintered compact.

[0010] Moreover, when it calcinates at temperature higher than 1900 degrees C, moreover it is because sintering will be inadequate, and eburnation will not be carried out but translucency will fall, if calcinating at the temperature of 1600-1900 degrees C calcinates at temperature lower than 1600 degrees C and is because abnormality grain growth arises, pore is incorporated in a grain and translucency falls, it is because evaporation of YAG arises and it becomes impossible to create a homogeneous sintered compact.

[0011] Furthermore, calcinating in a reducing atmosphere compares in atmospheric air, and it is H2. N2 It is because diffusion is quick, so the eburnation of a sintered compact can be attained easily. Vacuum firing is also good at the same reason.

[0012] For the YAG sintered compact of this invention, purity is aluminum 2O3 5m 2 of BET specific surface areas / more than 99.9% or more and g, respectively, for example. Powder and Y2 O3 About powder, it is aluminum 2O3. : Y2 O3 After preparing so that it may be set to 0.43:0.57, and mixing, temporary quenching is preferably carried out at 1000-1600 degrees C for about 2 hours for 0.5 hours or more. Temporary quenching is made to react to the condition in which the phase, i.e., YAM and YAG, before YAG-izing completely was intermingled. aluminum 2O3 Powder and Y2 O3 As for a powdered particle size, it is desirable that it is 2 micrometers or less, respectively in order to prevent abnormality grain growth of YAG.

[0013] And this is ground and it considers as raw material powder, and a predetermined solvent is added to this raw material powder, and preferential grinding of this is carried out to it by the pot mill, a tumbling mill, etc. As for the particle of temporary-quenching powder, it is preferably desirable that it is 1 micrometer or less 2 micrometers or less. Then, after drying this, a particle size regulation is carried out with 80-mesh pass. This is fabricated in the configuration of arbitration by the desired shaping means, for example, the die press, the cold isostatic press, extrusion molding, etc. For example, when based on the die press, it is 2.5 ton/cm3. It carries out above and the consistency of a generation form is raised as much as possible. The raw consistency of a Plastic solid is 2.1 g/cm3 in order to control the void in a sintered compact to the minimum. It is desirable to become the above.

[0014] And baking is performed at 1600-1900 degrees C for 2 to 10 hours in the vacuum ambient atmosphere whose degree of vacuum is 1x10 to 2 or more torrs. 1x10 to 3 or more torrs of a degree of vacuum are desirable. A certain constant temperature, for example, 1650 degrees C, has desirable 50-300 degrees C per hour, and 200-300 degrees C per hour of a programming rate are especially desirable. Then, it holds for 2 to 20 hours in order to equalize particle size. And a maximum temperature carries out a temperature up at 20 degrees C per hour preferably, and holds 100 degrees C or less per hour by the maximum temperature for 2 to 20 hours. Thus, a YAG sintered compact is obtained.

[0015] In addition, you may calcinate by reducing atmospheres, such as a hydrogen ambient atmosphere or nitrogen-gas-atmosphere mind, instead of calcinating in a vacuum ambient atmosphere.

[0016]

[Function] aluminum 2O3 Powder and Y2 O3 If powdered mixed powder is calcinated at the temperature of 1600 degrees C or more as it is, Although it becomes difficult for cubical expansion to arise, and for this to produce a void and a defect in a sintered compact, and to create a uniform sintered compact in case YAM generates from mixed powder, a crystal changes from YAM to YAG and it changes from YAM to YAG By the manufacture approach of the translucency YAG sintered compact of this invention aluminum 2O3 Powder and Y2 O3 Since temporary quenching of the powdered mixed powder was carried out at 1000-1600 degrees C and it was calcinated at 1600-1900 degrees C after this

Since the cubical expansion at the time of changing with 1000-1600-degree C temporary quenching from YAM to YAG can be produced, in baking after shaping, cubical expansion does not arise, and thereby, the void in a sintered compact and generating of a defect are controlled, and it becomes possible to create a uniform sintered compact. Thereby, the straight-line permeability of a light field can be made into 70% or more.

[0017] Moreover, according to this invention, like before, since it manufactures by general ordinary pressure baking not using the urea precipitation method of single crystal composition, HIP processing, a hotpress, yttrium ion, and aluminum ion etc., a translucency YAG sintered compact can be obtained cheaply and easily. Furthermore, since the transparent body is manufactured using a polycrystal YAG sintered compact, it can become a low price, reinforcement can be stabilized, the configuration of arbitration can be manufactured easily, and polish etc. can be processed easily.

[0018]

[Example] First, aluminum 2O3 99.9%, 5m 2 of BET specific surface areas / g, and whose diameter of average crystal grain purity is 0.7 micrometers as a start raw material, respectively 129g of powder, and Y2 O3 Easy [of the 171g of the powder] was carried out, high grade alumina-balls 600g and isopropyl alcohol (IPA) 300g as a binder were supplied to the poly pot, and preferential grinding was carried out to this by the tumbling mill for 24 hours. After making 325 meshes carry out through desiccation of the mixed thing, through and uniform powder were obtained for 80 meshes.

[0019] After carrying out temporary quenching at the temperature which shows this powder in Table 1 with an electric furnace at the temperature shown in Table 1, again, high grade alumina-balls 600g and isopropyl alcohol (IPA) 300g as a solvent were supplied to the poly pot, and preferential grinding was carried out by the tumbling mill for 24 hours. After making 325 meshes carry out through desiccation of the ground powder, through and uniform powder were obtained for 80 meshes. The Plastic solid of a three or more 2.5 g/cm raw consistency was created for this powder using the die press and a cold isostatic press. This Plastic solid was calcinated at the temperature of 1600-1900 degrees C for 2 to 20 hours by the burning temperature shown in Table 1, firing time, the programming rate, and the firing environments. Generation of YAG was checked when the obtained sintered compact was measured with X-ray diffractometer.

[0020] And after grinding the obtained sintered compact in thickness of 1mm, 1-micrometer diamond paste performed mirror plane finishing. The straight-line permeability of the light with a wavelength [of this sintered compact] of 600nm was measured with infrared spectrometer. In addition, the wavelength of a light field is 300-800nm. This experimental result is shown in Table 1.

[0021]

[Table 1]

試料 No,	仮焼温度 (℃)	焼成温度 (℃)	焼成時間 (時間)	昇温速度 (℃／H)	焼成 雰囲気	直線透過 率 (%)
＊1	——	1750	2	300	真空	52
2	1000	1750	2	300	真空	74
3	1300	1800	5	50	真空	76
4	1350	1600	20	100	真空	70
5	1350	1700	5	300	真空	77
6	1350	1750	2	300	真空	73
7	1350	1750	2	200	真空	75
8	1350	1750	2	100	真空	70
9	1350	1750	2	300	H_2	75
10	1350	1900	2	100	真空	74
11	1500	1750	2	300	真空	75
12	1600	1750	5	100	N_2	70
13	1600	1800	5	200	真空	70
＊14	800	1750	2	300	真空	55
＊15	——	1750	2	200	O_2	0.8

＊印は本発明の範囲外の試料を示す。

[0022] As for the YAG sintered compact of this invention, this experimental result shows that the straight-line permeability of a light field has 70% or more and the outstanding translucency. in addition, sample No. -- without it carries out temporary quenching of 1 and 15 -- aluminum 2O3 Powder and Y2 O3 It is the example which calcinated powder. Moreover, the programming rate in Table 1 is a programming rate to 1650 degrees C except for sample No.4. Moreover, although this invention person etc. conducted the experiment which performs temporary quenching at 1650 degrees C, it was not able to grind by the tumbling mill after temporary quenching in this case. Furthermore, although the experiment which calcinates at 1950 degrees C was conducted, it dissolved and the sample produced the crack during cooling.

[0023]

[Effect of the Invention] By the manufacture approach of the translucency YAG sintered compact of this invention, it is as explained in full detail above, 2Oaluminum3 powder and Y2 O3 Since temporary quenching was carried out at 1000-1600 degrees C and it calcinated at the temperature of 1600-1900 degrees C in the reducing atmosphere after this after mixing powder The cubical expansion at the time of changing with 1000-1600-degree C temporary quenching from YAM to YAG can be produced, in baking after shaping, cubical expansion cannot arise, thereby, the void in a sintered compact and generating of a defect can be controlled, and a uniform sintered compact can be created. Thereby, the straight-line permeability of a light field can be made into 70% or more, and the optimal ingredient for the aperture material for clocks, lamp tubing, accessories, etc. can be offered.

[Translation done.]